

Gas Generation Testing Of Plutonium Dioxide

Jon Duffey & Ron Livingston

Actinide Technology Section

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Why Conduct Gas Generation Tests?

- DOE-STD-3013-2000
 - H₂ gas generation described as the primary source of storage container pressurization
 - Limits oxide contents to 0.5 wt % water to prevent over pressurization
 - Requires processing at 950 °C for 2 hr to ensure moisture limit is met
- Observed pressures much less than predicted for complete decomposition of adsorbed moisture

Testing Objectives

- Measure gas generation rates as a function of:
 - moisture content
 - specific surface area
 - dose rate
 - fill gas composition
- Develop a technical basis to:
 - understand the impact of gas generation on long-term storage of oxides
 - support model development to predict gas generation phenomena (Paffett and Kelly)

PuO₂ Preparation

- Purified two isotopic mixtures by anion exchange
 - Weapons Grade (WG)
 - Mark 42 (Mk42 - 1.4X SA of WG)
- Precipitated Pu₂(C₂O₄)₃
- Calcined to oxide (SSA decreases with temperature)
 - 450 °C for 4 hr
 - 700 °C for additional 2 hr
 - 950 °C for additional 2 hr (Mk42 only)



PuO₂ Moisture Content

- Initial moisture content determined by TGA at 950 °C
- Additional moisture added by exposure to humid air at constant RH
 - 33 % RH (MgCl₂•6H₂O)
 - 75 % RH (NaCl)
 - 100 % RH (H₂O)
- Tracked weight change over time



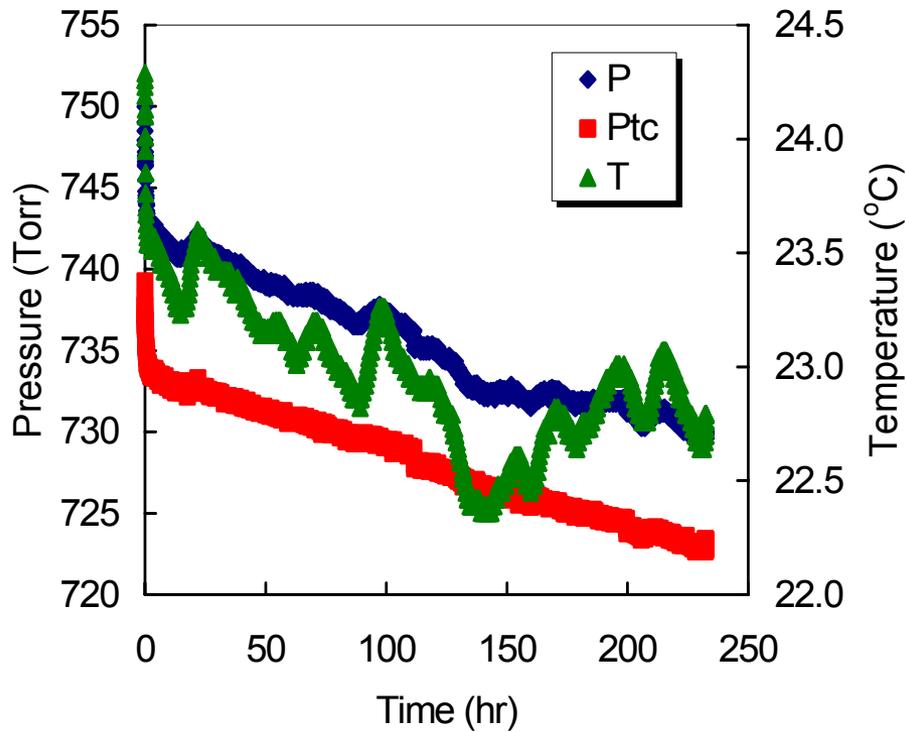
Gas Generation Tests

- Tests conducted with ≈ 9 g PuO_2 in SS vessels—free gas volume ≈ 25 mL
- Initial fill gas air, N_2 , Ar, or Ar/ H_2
- Recorded pressure and temperature for 1 to 3 weeks
- Sampled headspace gas and analyzed by GC for H_2 and O_2

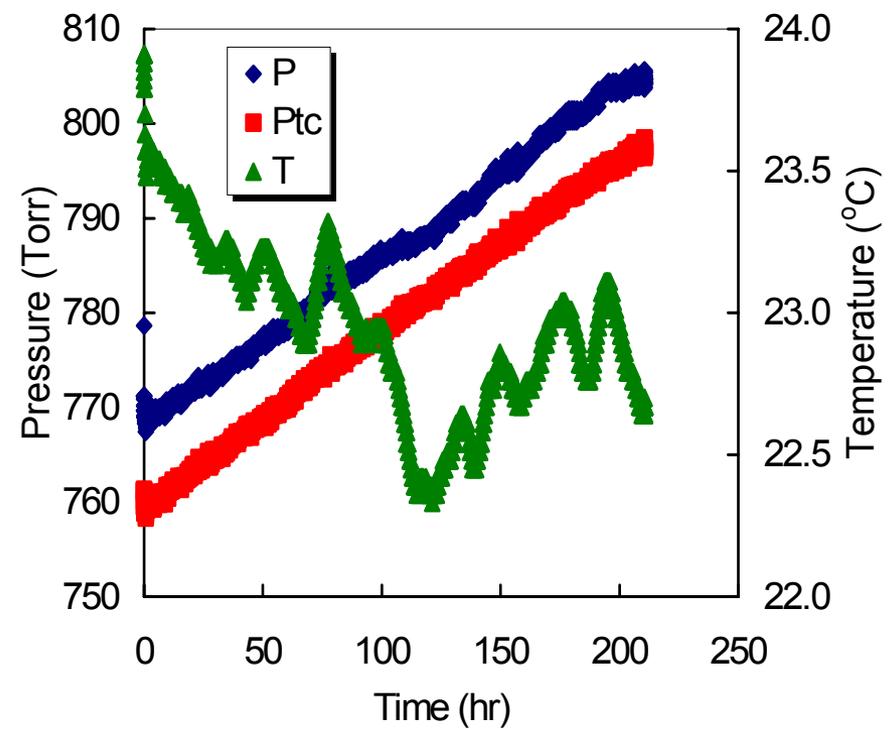


Effect of Moisture Content on Container Pressure

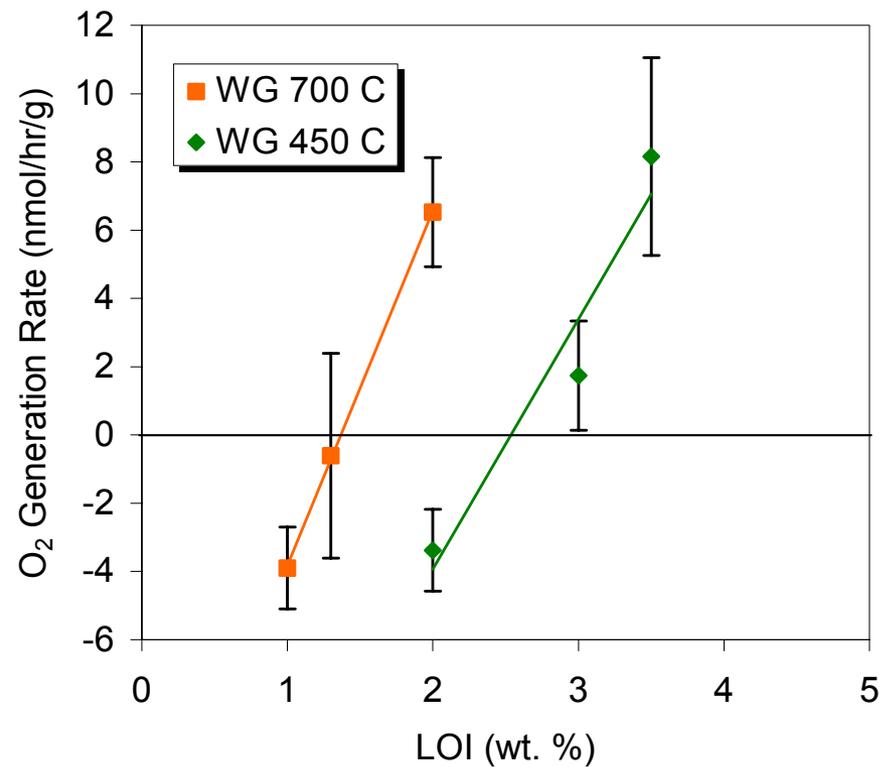
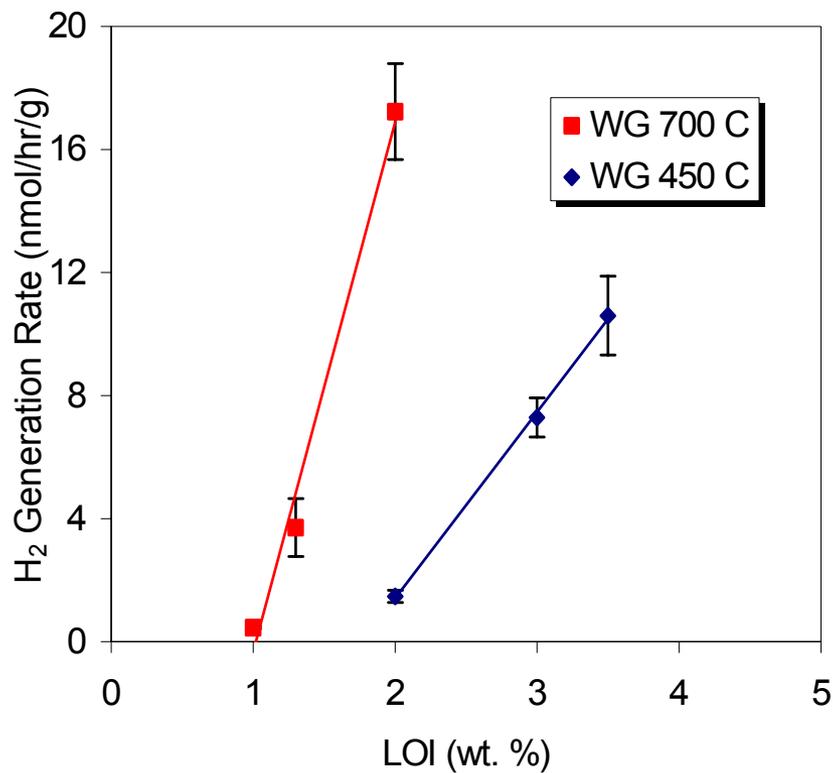
450 °C WG PuO₂ with 2.0 % LOI in Air



450 °C WG PuO₂ with 3.5 % LOI in Air



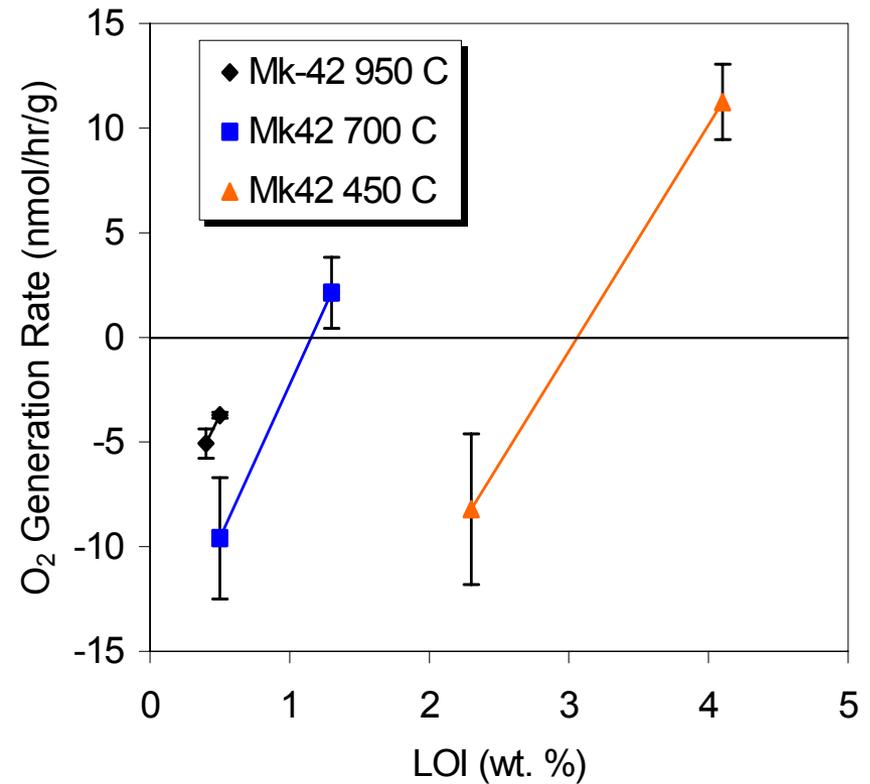
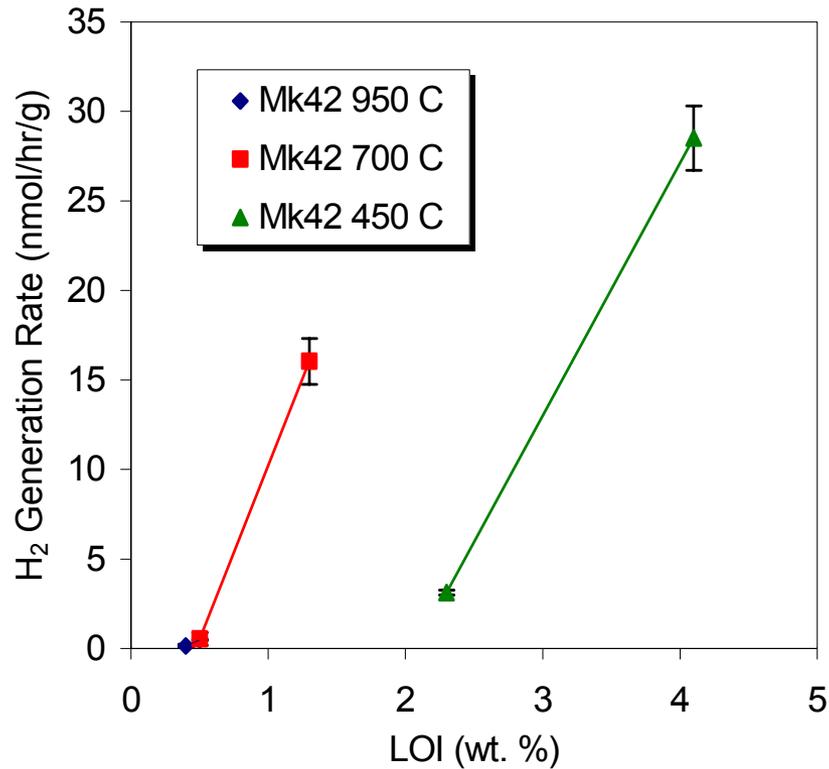
Rates Increase with %LOI and Calcination Temperature



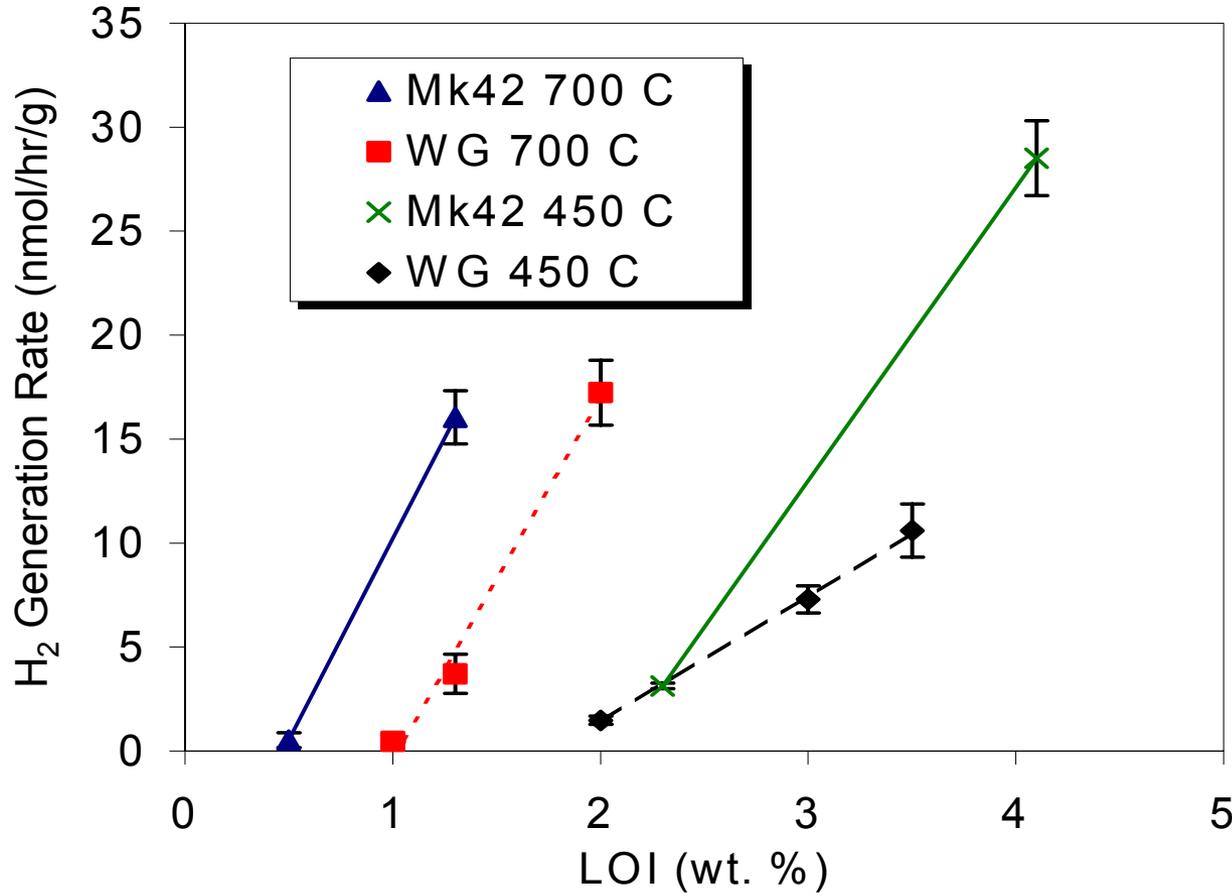
Results for WG PuO₂

Calcination Temperature (°C)	Water Content by LOI (wt. %)	Fill Gas ^a	Number of Replicates	Average H ₂ Generation Rate (nmol h ⁻¹ g ⁻¹)	Average O ₂ Generation Rate (nmol h ⁻¹ g ⁻¹)
450	2.0	air	2	1.5 ± 0.1	-3.4 ± 1.2
450	3.0	air	2	7.3 ± 0.7	1.7 ± 1.6
450	3.5	air	4	10.6 ± 1.3	8.2 ± 1.9
700	1.0	air	2	0.46 ± 0.04	-3.9 ± 1.2
700	1.3	air	2	3.7 ± 1.0	-1 ± 3
700	2.0	air	4	17.2 ± 1.6	6.5 ± 1.6
Blank ^b	N/A	Air	7	Not Detected	-0.2 ± 1.9

Rate Trends Similar for Mk42 and WG PuO₂



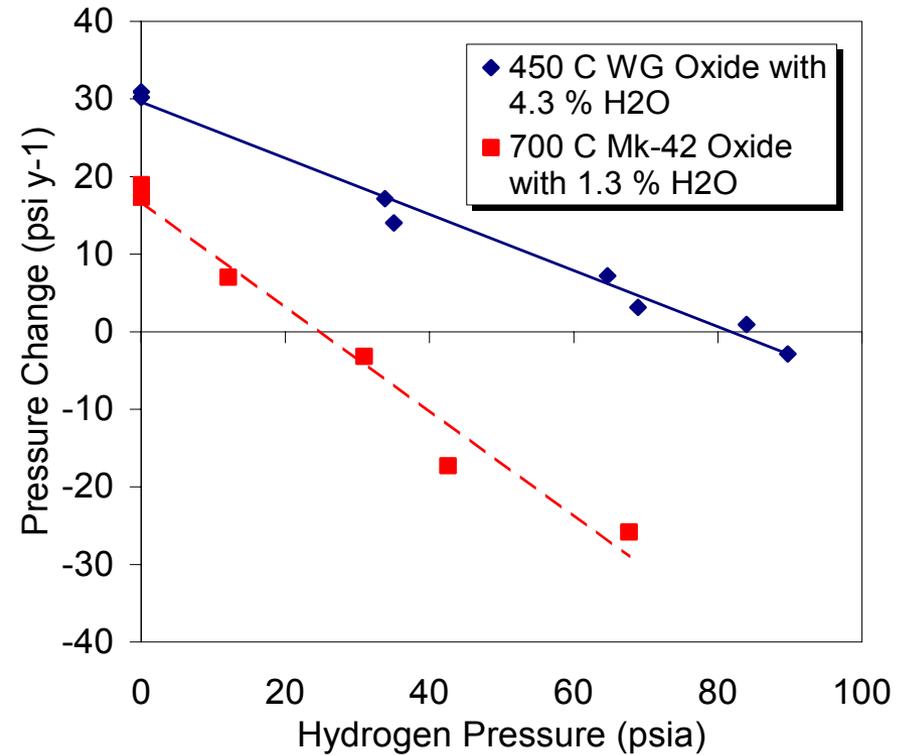
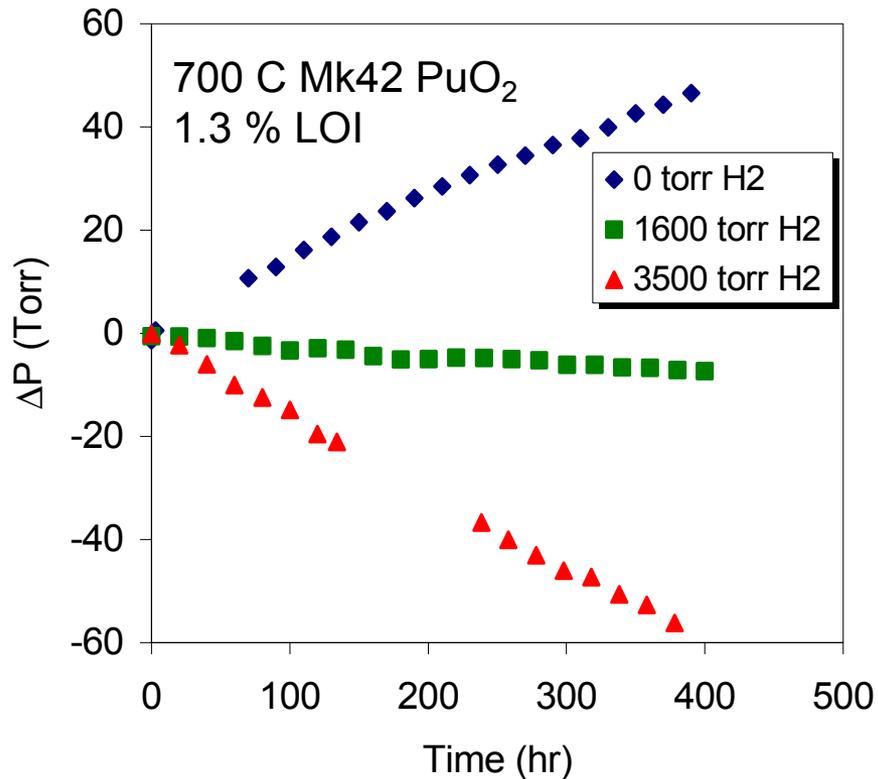
H₂ Generation Rates Increase with Dose Rate



H₂ Generation Rates Similar for Air, N₂, Ar; O₂ Rates Lower in Air

Calcination Temperature (°C)	Water Content by LOI (wt. %)	Fill Gas	Number of Replicates	Average H ₂ Generation Rate (nmol h ⁻¹ g ⁻¹)	Average O ₂ Generation Rate (nmol h ⁻¹ g ⁻¹)
450	2.3	air	3	3.13 ± 0.14	-8 ± 4
450	4.1	air	3	28.5 ± 1.8	11.2 ± 0.7
450	4.1	Ar	3	25.0 ± 1.6	16.4 ± 1.6
700	0.5	air	3	0.5 ± 0.4	-10 ± 3
700	1.3	air	3	16.0 ± 1.3	2.1 ± 0.8
700	1.3	N ₂	1	14.4 ± 1.6	6.3 ± 0.3
700	1.3	Ar	2	13 ± 6	7.2 ± 0.9
950	0.4	air	3	0.14 ± 0.10	-5.1 ± 0.7
950	0.5	air	2	0.47 ± 0.04	-3.72 ± 0.14
950	0.5	N ₂	1	0.25 ± 0.02	0.25 ± 0.02
950	0.5	Ar	2	0.22 ± 0.02	0.18 ± 0.02

Rate of Container Pressurization Decreases with H₂ Pressure



Conclusions

- Gas generation rates for PuO_2 :
 - increase with moisture content and dose rate
 - decrease with specific surface area
 - impacted by headspace gas composition
- H_2 generation rates slow at moisture contents < 0.5 wt %; O_2 is consumed
- Rate of container pressurization decreases with H_2 pressure
- Steady state reached at pressures much lower than supported by STD-3013 container design

Future Work

- Further evaluate the potential for reaching steady state pressure (October 2002)
- Measure effect of impurities on gas generation rates (February 2003)
- Investigate the impact of temperature on gas generation rates (February 2003)
- Measure oxide surface areas and improve moisture measurement capabilities (May 2003)

Acknowledgements

- DNFSB 94-1 Research and Development Project
- NMFA